

## Transplanting carbon nanotubes

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Current efforts of guided growth of carbon nanotubes alone cannot make large-scale and directed assembly of them. The *nanopelleting* concept overcomes this limitation by embedding carbon nanotubes in microscale pellets that can be transplanted readily. This technique includes vertical growth of carbon nanotubes, pellet casting, planarization, pellet separation, and transplantation. A specific manufacturing process is developed and tested with favorable results. This technology will enable directed assembly of carbon nanotubes in a long-range order. © 2004 American Institute of Physics. [DOI: 10.1063/1.1836865]

Carbon nanotubes (CNTs) elicited significant attention upon their discovery. There has been continuous interest and research covering the synthesis and potential applications of single- and multiwalled carbon nanotubes. Widespread use of CNTs is predicated on the development of robust large-scale manufacturing techniques. There remain, however, few feasible methods for the large-scale handling of geometrically uniform CNTs,<sup>1,2</sup> which has limited their integration into successful commercial applications to date.

The key challenges to developing robust manufacturing techniques can be grouped into three categories: Growth, handling, and functionalization. The growth is carried out using either of catalytic methods with chemical vapor deposition (CVD), both thermal and plasma-enhanced (PE), or with noncatalytic methods, such as arc evaporation or laser ablation. Previous research on CNT growth using PE-CVD systems<sup>3-8</sup> has demonstrated the capability of aligned growth of CNTs, both individually and in clusters, but has not demonstrated over large areas. A challenge with these growth methods of aligned CNTs is to cover areas larger than several square centimeters. Consequently, the current efforts for large-scale CNT assembly rely on liquid dispersions<sup>9-11</sup> that do not provide deterministic control over individual CNT alignment or position during assembly. Recently, researchers have reported manipulation of individual CNTs via atomic force microscope probe tips,<sup>12,13</sup> electric field,<sup>14</sup> and surface forces.<sup>15</sup> But all these methods have inherently low yield and throughput for large-scale device fabrication.

In this letter, we demonstrate a process<sup>16</sup> for transplanting CNTs, termed *nanopelleting*, which provides specific control over individual CNTs in length, alignment, and position over large areas. Conceptually, a nanopellet consists of a CNT (or CNTs) embedded within a microscale block. The block serves as a microscale transport vehicle, or carrier, for

the nanostructure, facilitating the handling and assembly of CNTs. Further, the embedded CNT (or CNTs) can also be trimmed within the pellet via a chemical mechanical polishing (CMP) process. Nanopelleting thereby provides a functional periodicity to individual CNT (or CNTs), uncoupled from spatial and temporal process fluctuations normally experienced in CNT growth. Moreover, nanopellets provide a seeding mechanism where CNTs can be grown and subsequently harvested; this enhances control over yield, enabling the fabrication of devices with large areas of high-quality CNTs. Consider the case of growing healthy flowers in an ideal green house, one stem in one pot, and transplanting them into arbitrary locations by simply relocating individual pots. Nanopelleting is similar to this case, but in microscale.

In the design of nanopellets, functional requirements for the CNTs assembly are laid out. Specifically, the CNT (or CNTs) should be embedded into a pellet with known (vertical) alignment. Further, the pellet itself should be of uniform length, selectively releasable from the substrate along with the embedded CNTs when they are harvested, and the pellet body material should be selectively removable to expose the CNTs when it is necessary. Finally, the pellets should have the required features to enable self-assembly onto an acceptor substrate. The initial target of this research was to satisfy these requirements by demonstrating the release and transplantation of a pellet with embedded CNTs. A coin-type pellet is designed, 100  $\mu\text{m}$  in diameter and 2  $\mu\text{m}$  in depth.

To fabricate nanopellets, standard microelectronics fabrication processes and tools are utilized. The overall process for fabricating nanopellets, shown in Fig. 1, utilizes silicon trenches to cast polymer into the pellet bodies. The CNTs are grown on the catalyst patch at the bottom of the trenches to form a 8  $\mu\text{m}$  diameter bundle of vertically aligned nanotubes [Fig. 2(b)]. An epoxy polymer is then cast onto the substrate, encapsulating the CNTs, and the surface is planarized to remove excess polymer and trim the CNTs to a uniform length. The pellets are then released from the silicon substrate.

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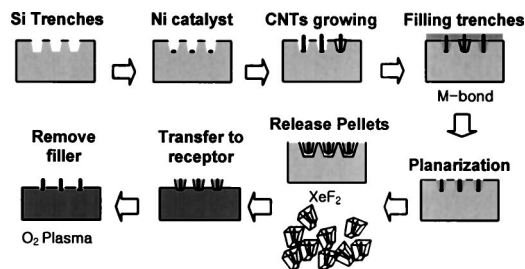


FIG. 1. An overview of nanopelleting processes. The pellets are fabricated by etching trenches, growing CNTs with vertical alignment in the trenches, then spin casting an epoxy polymer, and planarizing the substrate to create isolated pellets with uniform-length CNTs. The pellets can then be released, harvested, and transplanted in large scale.

Fabricating trenches with small catalyst patches at their bottom center is straightforward. But the depth of the trench is governed by the focal length of the optical lithography, which limits the aspect ratio of nanopellets. The trenches are etched using reactive ion etching (but could also be KOH etched to achieve sloping sidewalls) and patterned positive photoresist. CNTs are grown on catalytic patches via PE-CVD.<sup>3,4</sup> Control over the location and quantity of the CNTs is possible by controlling the catalyst patch size and location. The catalyst patches used are 15 nm thick nickel deposited via electron-beam (e-beam) evaporation and patterned to 5–10  $\mu\text{m}$  diameter dots using optical lithography. CNT growth was conducted with a 20 nm  $\text{SiO}_2$  buffer layer under the nickel patch. The PE-CVD chamber run an acetylene/ammonia gas mixture (80 sccm/160 sccm) with a heated cathode at 500  $^\circ\text{C}$  and a dc power source for plasma ignition operating at  $\sim 515$  V.

The PE-CVD process resulted in patterned growth of vertically aligned nanotubes only at the catalyst patch at the bottom of a trench, as shown in Fig. 2, which is consistent with prior CVD work.<sup>3,4</sup> Stress fluctuation developed around catalyst particles by the electric field can modulate the diffusion rate of carbon atoms, so as to prevent the deviation of the direction of CNT growth from the electric-field direction.<sup>17</sup> Then, an epoxy resin is spin coated to fill the trenches. The filler used in our experiments is a two-part epoxy, 610 M-Bond sold by SPI Supplies, spun on, and cured at 175  $^\circ\text{C}$  for 1 h. There is no visible adverse effect on the CNT alignment after filling the trenches with the epoxy polymer, which fully embeds the CNT cluster. Then, the substrate is planarized on a standard dual-rotor CMP machine at 35–50 rpm rotor speeds and 5–10 psi pad pressures. This is done on 1  $\text{cm}^2$  pieces adhered to the rotor head by wetting the back side of the die and relying on surface tension with the rotor head's rubber pad. The CMP process provides a reliable means for trimming buried CNTs as shown in Fig. 3.

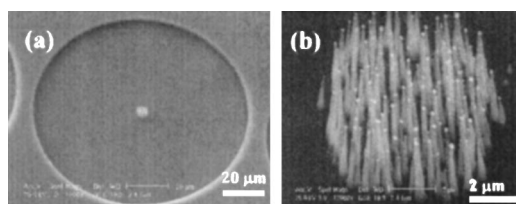


FIG. 2. A trench (100  $\mu\text{m}$  diameter, 2  $\mu\text{m}$  depth) on a silicon wafer with an 8  $\mu\text{m}$  diameter CNT bundle at center. The vertically grown CNTs can be seen clearly in (b), with nickel dots at the tip demonstrating tip-growth mode.

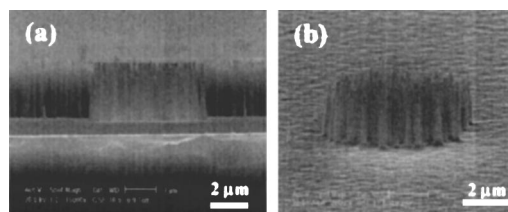


FIG. 3. Trimmed CNTs via CMP process: (a) A side view of the planarized CNTs after the removal of the epoxy body via  $\text{O}_2$  plasma. (b) An oblique view of the planarized CNTs after the removal of the epoxy body via  $\text{O}_2$  plasma.

Depending on the initial thickness of the epoxy, this step may take time on the order of 60 min, with a faster material removal rate at lower pressures and higher rotor speeds. After planarization, the pellets are released using a  $\text{XeF}_2$  etch, which selectively releases the epoxy pellet from the silicon substrate along with the embedded CNTs. Selective removal of the epoxy to expose CNTs is also achieved via oxygen plasma ashing as shown in Figs. 3(a) and 3(b). To confirm the resistance of CNTs to the processes selected to release the pellets from a silicon substrate as well as removing the filler material, we tested the effect of oxygen plasma and  $\text{XeF}_2$  on CNTs. The results shown in Figs. 4(a) and 4(b) confirm that CNTs are not attacked by oxygen plasma after 30 min of exposure, while the M-bond epoxy is removed. Additionally, the results confirm that  $\text{XeF}_2$  does not attack the CNTs and can therefore be used to release pellets.

The final step of the process is to transplant the released pellets to a substrate (receptor). We have positioned pellets onto an acceptor wafer surface, prepatterned in the T-shape, as shown in Fig. 5(b). Manual translation and alignment is carried out on a microprobe station, where 12  $\mu\text{m}$  sharp tips mounted onto  $x/y/z$  stages are used to push the pellets into position. The circular pellets are pushed and dropped into shallow trenches [Fig. 5(a)], which are etched slightly larger (110  $\mu\text{m}$ ) than the diameter of the pellets (100  $\mu\text{m}$ ) and bottom coated with indium to be heated above its melting point to secure the pellets in place. Exposing CNT bundles requires one to solidly anchor CNTs to the acceptor substrate surface and to remove the pellet epoxy material. Simplified CNT anchoring experiments were conducted with an acceptor substrate having a 50 nm thick evaporated indium layer. A CNT pellet is bonded by placing it on the acceptor wafer surface and heating the wafer to 200  $^\circ\text{C}$  for 30 min. The pellet exhibited fair adhesion to the surface, allowing the wafer to be flipped upside down without displacing the pellet. The bonded pellet is then exposed to oxygen plasma for 30 min, removing the pellet material but leaving the CNTs and indium surface intact.

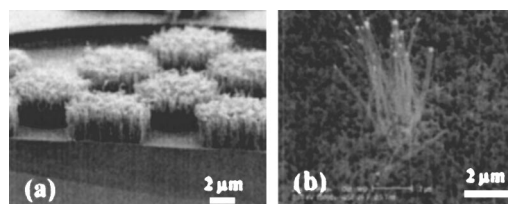


FIG. 4. The results of the CNT selectivity experiments: (a) Showing densely packed CNT bundles that were embedded in epoxy, not planarized and oxygen plasma ashed, and (b) showing a loose bundle of CNTs, not planarized, exposed to  $\text{XeF}_2$  gas.

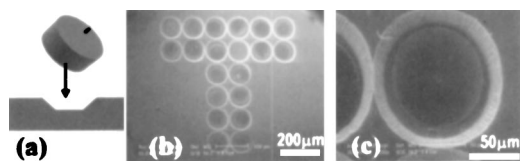


FIG. 5. Transplanting of CNTs: (a) A schematic view of the concept of transplanting nanopellets, (b) transplanted pellets arranged into receptor trenches, forming a T shape, and (c) a nanopellet with CNTs in center before O<sub>2</sub> ashing.

We have demonstrated the feasibility of the nanopelleting concept as a method for transplanting CNTs. The results support the merit of nanopelleting as a means of deterministic assembly of CNTs. Further works on functionalizing nanopellets is necessary to fully harness this technique. Self-assembly methods for microstructures, including fluidic and cellular self-assembly<sup>18,19</sup> are particularly promising together with the nanopelleting process. Also of interest for this process is the capability to make pellets with bundles of CNTs or with individual CNTs. Prior reports on individual nanotube growth<sup>4,20</sup> have demonstrated this is feasible with submicron-sized nickel catalyst sites. Accordingly, we have patterned submicron scale catalyst patches using e-beam lithography and are targeting the growth of individual CNTs to make high-aspect-ratio cylindrical nanopellets, called nanocandles.

Further, the harvesting of nanopellets allows for the development of applications with large-scale assemblies of CNTs. Applications that are particularly well suited to nanopelleting are those that require large expanses of arrayed CNTs with specific geometries, alignment, and location. Examples of such applications include field emission displays, where even a relatively small display of several square inches would require vast numbers of ordered CNTs. Other potential applications that may be enabled by this technique but are yet underexplored include the use of CNT arrays for nanolithography using photo/thermal/electron energy beams, as well as structural applications, such as carbon nanocomposite interconnects. Moreover, given the broader utility of the nanopelleting concept in terms of multiscale manufactur-

ing, nanopelleting can be used more broadly for a variety of nanostructures and their applications.

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- <sup>1</sup>P. M. Ajayan and O. Z. Zhou in *Carbon Nanotubes: Synthesis, Structure, Properties, and Applications*, Topics in Applied Physics Vol. 80, edited by M. S. Dresselhaus, G. Dresselhaus, and P. Avouris (Springer, Berlin, Germany, 2001), p. 391.
- <sup>2</sup>P. J. F. Harris, *Carbon Nanotubes and Related Structures: New Materials for the Twenty-First Century* (Cambridge University Press, Cambridge, UK, 1999).
- <sup>3</sup>Z. F. Ren, Z. P. Huang, J. W. Xu, J. H. Wang, P. Bush, M. P. Siegal, and P. N. Provencio, *Science* **282**, 1105 (1998).
- <sup>4</sup>Z. F. Ren, Z. P. Huang, D. Z. Wang, J. G. Wen, J. W. Xu, J. H. Wang, L. E. Calvet, J. Chen, J. F. Klemic, and M. A. Reed, *Appl. Phys. Lett.* **75**, 1086, (1999).
- <sup>5</sup>H. Wang, J. Lin, C. H.A. Huan, P. Dong, J. He, S. H. Tang, W. K. Eng, and T. L.J. Thong, *Appl. Surf. Sci.* **181**, 248 (2001).
- <sup>6</sup>J. I. Sohn and S. Lee, *Appl. Phys. A: Mater. Sci. Process.* **74**, 287 (2002).
- <sup>7</sup>Y. Tu, Z. P. Huang, D. Z. Wang, J. G. Wen, and Z. F. Ren, *Appl. Phys. Lett.* **80**, 4018 (2002).
- <sup>8</sup>S. Huang, L. Dai, and A. Mau, *Physica B* **323**, 333 (2002).
- <sup>9</sup>Y. Huang, X. Duan, Q. Wei, and C. M. Lieber, *Science* **291**, 630 (2001).
- <sup>10</sup>E. Valentin, S. Auvray, A. Filoramo, A. Ribayrol, M. Foggman, L. Capes, J.-P. Bourgoin, and J.-N. Patillon, *Mater. Res. Soc. Symp. Proc.* **772**, 201 (2003).
- <sup>11</sup>S. J. Oh, Y. Cheng, J. Zhang, H. Shimoda, and O. Zhou, *Appl. Phys. Lett.* **82**, 2521 (2003).
- <sup>12</sup>T. Hertel, R. Martel, and P. Avouris, *J. Phys. Chem. B* **102**, 910 (1997).
- <sup>13</sup>S. K. Kim, S. K. Lim, I. B. Lee, K. H. An, D. J. Bae, S. Choi, J. -E. Yoo, and Y. H. Lee, *Rev. Sci. Instrum.* **74**, 4021 (2003).
- <sup>14</sup>J. Chung, K. Lee, J. Lee, and R. Ruoff, *Langmuir* **20**, 3011 (2004).
- <sup>15</sup>S. Rao, L. Huang, W. Setyawan, and S. Hong, *Nature (London)* **425**, 36 (2003).
- <sup>16</sup>S. G. Kim, U.S. Patent application No. 60/417, 959 (2002).
- <sup>17</sup>V. I. Merkulov, A. V. Melechko, M. A. Guilorn, D. H. Lowndes, and M. L. Simpson, *Appl. Phys. Lett.* **79**, 2970 (2001).
- <sup>18</sup>U. Srinivasan, D. Liepmann, and R. T. Howe, *J. Microelectromech. Syst.* **10**, 17 (2001).
- <sup>19</sup>G. M. Whitesides, *Sci. Am.* **285**, 78 (2001).
- <sup>20</sup>V. I. Merkulov, D. H. Lowndes, Y. Y. Wei, G. Eres, and E. Voelkl, *Appl. Phys. Lett.* **76**, 3555 (2000).